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Uppsala University, Uppsala, Sweden

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On leave from: Department of Physics, Faculty of Science, University of Tokyo, Tokyo, Japan.

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1. INTRODUCTION

A single-determinant form for wave functions has been used extensively in the quantum mechanics of many-electron systems.

In the usual Hartree-Fock method, single-determinant wave functions are used with a restriction that two electrons with spins α and β are put into the same space orbital. A single-determinant wave function with this restriction is an eigenfunction of the total spin operator S^2 . The Hartree-Fock method has proved to be very useful in the theory of atoms, molecules and solids.

In the unrestricted Hartree-Fock method, single-determinant wave functions without the above mentioned restriction are used. This allows us to treat, in a compact form, the exchange polarization and the correlation of electrons with antiparallel spins. However, the unrestricted Hartree-Fock method has a disadvantage. Wave functions used in the method are in general not eigenfunctions of the total spin but are linear combinations of eigenfunctions which have different eigenvalues.

It is of some interest to see how much of each spin eigenfunction is contained in the single-determinant wave function.

2. FORMULATION OF THE PROBLEM

Any antisymmetric wave function of an N-electron system can be written in the following form,

$$\Phi(\xi_1, \xi_2, \cdots, \xi_N) = \mathcal{A}\left(\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)\Theta(\sigma_1, \sigma_2, \cdots, \sigma_N)\right), \quad (2.1)$$

where ξ_i stands for the space and spin coordinates I_i and σ_i respectively of the i-th electron. A is the idempotent antisymmetrizing operator. By using permutation operators P and their parities ϵ_p , the antisymmetrizing operator A is expressed as

$$A = \frac{1}{N!} \sum_{P} \varepsilon_{P} P. \qquad (2.2)$$

The wave function Φ is in general a linear combination of pure spin states:

$$\Phi = \sum \Phi_{S,M} \qquad , \tag{2.3}$$

where $\Phi_{S,M}$ is an eigenfunction of S^2 and S_Z with the eigenvalues S(S+1) and M respectively ($\hbar=1$).

This decomposition is of physical importance if the Hamiltonian does not involve spin operators. An expectation value of a spin-free operator f can be expressed as

$$\langle f \rangle = \frac{\langle \Phi, f \Phi \rangle}{\langle \Phi, \Phi \rangle}$$

$$= \sum_{S,M} \omega_{S,M} \langle f \rangle_{S,M} , \qquad (2.4)$$

where

$$\omega_{S,M} = \frac{(\Phi_{S,M}\Phi_{S,M})}{(\Phi,\Phi)} \ge 0 , (\sum_{S,M} \omega_{S,M} = 1)$$
 (2.5)

and

$$\langle f \rangle_{S,M} = \frac{\langle \Phi_{S,M}, f \Phi_{S,M} \rangle}{\langle \Phi_{S,M}, \Phi_{S,M} \rangle}$$
(2.6)

when $<\Phi_{S,M}$, $\Phi_{S,M}$ > is not zero. When the Hamiltonian of the system is spin-free, we have

$$E = \sum_{S,M} \omega_{S,M} E_{S,M} . \qquad (2.7)$$

This equation shows that at least one of the energy expectation values $E_{S,M}$ is lower than E unless all $E_{S,M}$ are equal to E. By selecting from Φ a suitable spin component $\Phi_{S,M}$, we have a wave function which is not only a spin eigenfunction but which has a lower energy expectation value.

The analysis is also useful in interpreting the function Φ , (2.1). This is in some cases (e.g. a single Slater determinant) much easier to handle than its components $\Phi_{S,M}$. If we know the values of $\omega_{S,M}$ and $\langle f \rangle_{S,M}$, we can better interpret the nature of the simple form (2.1). One of the basic problems here is to determine the weight $\omega_{S,M}$.

In the following we shall investigate a special case in which the spin part Θ of the wave function (2.1) is a simple product of spin functions $\gamma_i(\sigma_i)$ which are either $\alpha(\sigma_i)$ or $\beta(\sigma_i)$:

$$\theta (\sigma_1, \sigma_2, \cdots, \sigma_N) = \gamma_1 (\sigma_1) \gamma_2 (\sigma_2) \cdots \gamma_N (\sigma_N). \qquad (2.8)$$

The spin function Θ is an eigenfunction of S_Z . If we denote the number of a and β functions in (2.8) by N_a and N_β respectively, the eigenvalue of S_Z (M) is expressed as

$$M = \frac{1}{2} (N_{\alpha} - N_{\beta}) . \qquad (2.9)$$

In order to evaluate $\omega_{S,M}$, it is convenient to introduce the spin operator $O_{S,M}$ which projects out the component of the pure spin state:

$$\{S^2 - S(S+1)\} O_{SM} = 0$$
,
 $\{S_Z - M\} O_{S,M} = 0$,
 $\sum_{S,M} O_{S,M} = 1$. (2.10)

We note that this operator works only on the spin part of a wave function. For any wave function

$$\Phi = \sum_{i} c_{i} \Psi_{i}(\mathbf{r}_{1}, \mathbf{r}_{2}, \cdots, \mathbf{r}_{N}) \Theta_{i}(\sigma_{1}, \sigma_{2}, \cdots, \sigma_{N}) ,$$

OS. M D is expressed as

$$O_{S,M}\Phi = \sum_{i} c_{i} \Psi_{i} (O_{S,M}\Theta_{i})$$
.

Since the wave function under consideration is an eigenfunction of $S_{\mathbb{Z}}$ with the eigenvalue M, we shall drop the subscript M in the following unless it causes some ambiguity.

The weight ω_S for the wave function Φ can be written as

$$\omega_{S} = \frac{\langle O_{S} \Phi, O_{S} \Phi \rangle}{\langle \Phi, \Phi \rangle} = \frac{\langle \Psi \Theta, O_{S} * \Psi \Theta \rangle}{\langle \Psi \Theta, A \Psi \Theta \rangle}$$

$$= \frac{\sum_{P} \varepsilon_{P} \langle \Psi, P^{x} \Psi \rangle \langle \Theta, O_{S} P^{\sigma} \Theta \rangle}{\sum_{P} \varepsilon_{P} \langle \Psi, P^{x} \Psi \rangle \langle \Theta, P^{\sigma} \Theta \rangle} . \qquad (2.11)$$

where P^X and P^{σ} denote the corresponding permutations of the space and the spin coordinates respectively. Similarly we obtain the expectation value of a spin-free operator f,

$$\langle f \rangle_{S} = \frac{\langle O_{S} \Phi, f O_{S} \Phi \rangle}{\langle O_{S} \Phi, O_{S} \Phi \rangle} = \frac{\langle \Psi \Theta, f O_{S} A \Psi \Theta \rangle}{\langle \Psi \Theta, O_{S} A \Psi \Theta \rangle}$$

$$= \frac{\sum_{P} \varepsilon_{P} \langle \Psi, f P^{X} \Psi \rangle \langle \Theta, O_{S} P^{O} \Theta \rangle}{\sum_{P} \varepsilon_{P} \langle \Psi, P^{X} \Psi \rangle \langle \Theta, O_{S} P^{O} \Theta \rangle} . \tag{2.12}$$

We shall derive an explicit formula for $<\Theta$, $O_SP^{\sigma_\Theta}>$ in the next section. In sections 4 and 5, the weights ω_S derived from a single Slater determinant are given, and the behaviour of the ω_S -values for large N is discussed.

3. CALCULATIONS OF
$$\langle \Theta, O_S P^{\sigma} \Theta \rangle$$

Because we assumed the form (2.8) for the spin part Θ , for any permutation P we can find a permutation Q(P) which brings Θ and $P^{\sigma}\Theta$ into the following forms:

$$Q^{\circ} \Theta = \alpha(1)\alpha(2) \cdots \alpha(n+M)\beta(n+M+1) \cdots \beta(2n) \equiv f_{0} , \qquad (3.1)$$

$$Q^{\circ} P^{\circ} \Theta = \alpha(1) \cdots \alpha(n+M-i)\beta(n+M-i+1) \cdots \beta(n+M) \times \alpha(n+M+1) \cdots \alpha(n+M+i)\beta(n+M+i+1) \cdots \beta(2n)$$

$$\equiv f_{i} , \qquad (2n = N) . \qquad (3.2)$$

Here the integer i(P) is the number of a-functions in Θ which are changed to β -functions in $P^{\sigma}\Theta$. The number i(P) is uniquely determined by the given permutation P.

Using the commutability of $\,O_{\mbox{\scriptsize S}}\,$ and $\,\mbox{\scriptsize Q}^{\,\mbox{\scriptsize \sigma}}\,$, we obtain

$$\langle \Theta, O_{S} P^{\sigma} \Theta \rangle = \langle Q^{\sigma} \Theta, Q^{\sigma} O_{S} P^{\sigma} \Theta \rangle$$

$$= \langle Q^{\sigma} \Theta, O_{S} Q^{\sigma} P^{\sigma} \Theta \rangle$$

$$= \langle f_{0}, O_{S} f_{i} \rangle \equiv c_{S, i} \qquad (3.3)$$

In order to calculate the value $c_{S,i}$, it is convenient to divide the total number of electrons into four groups A, B, C and D. A, B, C and D stand for the first n+M-i electrons, the second i electrons, the third i electrons and the last n+M-i electrons, respectively:

- A 1, 2, ..., n + M i,
- B n + M i + 1, n + M i + 2, ..., n + M
- C n + M + 1, n + M + 2, ..., n + M + i.
- D n + M + i + 1, n + M + i + 2, ..., 2n.

For example when we write CD, this means the combined groups of C and D, i.e. the last n - M electrons.

We introduce the symbol $Y_K(s,m;\mu)$ for one element of an orthonormal complete set of simultaneous spin eigenfunctions of S^2 and S_Z with the eigenvalues s(s+1) and m respectively. K denotes an electron system which can be any of the groups defined above. μ specifies one of the spin functions with common s and m, to differentiate degenerate functions. We adopt the usual convention for the relative phase of these functions s

$$(S_x \pm i S_y) Y_K(s,m;\mu) = \sqrt{(s \mp m)(s \pm m + 1)} Y_K(s,m \pm 1;\mu)$$
 (3.4)

As the element of the set which has the highest eigenvalue of S^2 (s = $N_K/2$, N_K is the number of electrons in the group K), we choose the following function:

$$Y_{K}(N_{K}/2,N_{K}/2) = \alpha \alpha \cdots \alpha. \qquad (3.5)$$

We may drop μ in this case since (3.5) is the only function in the set with the eigenvalues $s = m = N_K/2$. From (3.4) and (3.5), we obtain

$$Y_{K}(N_{K}/2,-N_{K}/2)=\beta\beta\cdots\beta. \tag{3.6}$$

An orthonormal set of spin functions of the system ABCD can be obtained by coupling Y_{AB} and Y_{CD} in the following manner:

$$V_{ABCD}(s,m;\mu) = Y_{ABCD}(s,m;s's''\mu',\mu'')$$

= $\sum_{m'm''} Y_{AB}(s',m';\mu') Y_{CD}(s',m';\mu') \times \times (s',m',s'',m''|s',s'',s,m|).$ (3.7)

Here (s,m,s,m, s,s,s,m) is the vector coupling coefficient 2):

$$(s',m', s',m'| s',s'',s,m) = \delta(m'+m''-m') \times \left\{ \frac{(2s+1)(s'+s''-s)!(s'-m')!(s''-m'')!(s+m)!(s-m)!}{(s'+s'+s+1)!(s'-s'+s)!(-s'+s'+s)!(s'+m')!(s''+m'')!} \right\}^{1/2} \times$$

$$\times \sum_{v} (-1)^{v+s'-m'} \frac{(s'+m'+v)!(s'+s-m'-v)!}{v!(s'-m'-v)!(s-m-v)!(s''-s+m'+v)!}$$
(3.8)

Since

$$O_{S,M} = \sum_{\mu} Y_{ABCD}(S, M; \mu) \langle Y_{ABCD}(S, M; \mu), (3.9)$$

we obtain

$$c_{S,i} = \sum_{\mu} \langle f_0, Y_{ABCD}(S, M; \mu) \rangle \langle Y_{ABCD}(S, M; \mu), f_i \rangle$$
 (3.10)

The functions f_0 and f_i are expressed as

$$f_0 = Y_{AB}(\frac{n+M}{2}, \frac{n+M}{2}) Y_{CD}(\frac{n-M}{2}, -\frac{n-M}{2})$$
 (3.11)

and

$$f_{i} = V_{A}(\frac{n+M-i}{2}, \frac{n+M-i}{2}) \quad V_{B}(\frac{i}{2} - \frac{i}{2}) \times V_{C}(\frac{i}{2}, \frac{i}{2}) \quad V_{D}(\frac{n-M-i}{2}, -\frac{n-M-i}{2})$$
(3.12)

Therefore, the terms of the right side of (3.10) vanish except for the following YABCD:

$$V_{ABCD}(S,M; \frac{n+M}{2}, \frac{n-M}{2}) = \sum_{m',m''} V_{AB}(\frac{n+M}{2}, m') V_{CD}(\frac{n-M}{2}, m'') \times (\frac{n+M}{2}, m', \frac{n-M}{2}, m', \frac{n-M}{2}, m'') \times (\frac{n+M}{2}, m', \frac{n-M}{2}, m', \frac{n-M}{2}, m'') \times (\frac{n+M}{2}, m', \frac{n-M}{2}, m', \frac{n-M}{2}, m', \frac{n-M}{2}, m'') \times (\frac{n+M}{2}, m', \frac{n-M}{2}, m', \frac{n-M}{2}, m', \frac{n-M}{2}, m'') \times (\frac{n+M}{2}, m', \frac{n-M}{2}, m$$

Here

$$V_{AB}(\frac{n+M}{2}, m) = \sum_{m'm'} V_{A}(\frac{n+M-i}{2}, m') V_{B}(\frac{i}{2}, m') \times (\frac{n+M-i}{2}, m'; \frac{i}{2}, m'; \frac{n+M-i}{2}, \frac{i}{2}, \frac{n+M}{2}, m)$$
(3.14)

and

$$V_{CD}(\frac{n-M}{2}, m) = \sum_{mm'} V_{C}(\frac{i}{2}, m') Y_{D}(\frac{n-M-i}{2}, m'') \times$$

$$\times (\frac{i}{2}, m', \frac{n-M-i}{2}, m'') \frac{i}{2}, \frac{n-M-i}{2}, \frac{n-M}{2}, m).$$
(3.15)

Using (3.8), (3.11), (3.12), (3.13), (3.14) and (3.15), we find

$$\begin{split} c_{S,i} &= \langle f_0, Y_{ABCD}(S, M : \frac{n+M}{2}, \frac{n-M}{2}) \rangle \langle Y_{ABCD}(S, M : \frac{n+M}{2}, \frac{n-M}{2}), f_i \rangle \\ &= (\frac{n+M}{2}, \frac{n+M}{2}, \frac{n-M}{2}, -\frac{n-M}{2} \mid \frac{n+M}{2}, \frac{n-M}{2}, S, M) \times \\ &\times (\frac{n+M-i}{2}, \frac{n+M-i}{2}, \frac{i}{2}, -\frac{i}{2} \mid \frac{n+M-i}{2}, \frac{i}{2}, \frac{n+M}{2}, \frac{n+M-2i}{2}) \times \\ &\times (\frac{i}{2}, \frac{i}{2}, \frac{n-M-i}{2}, -\frac{n-M-i}{2} \mid \frac{i}{2}, \frac{n-M-i}{2}, \frac{n-M}{2}, -\frac{n-M-2i}{2}) \times \\ &\times (\frac{n+M}{2}, \frac{n+M-2i}{2}, \frac{n-M}{2}, -\frac{n-M-2i}{2} \mid \frac{n+M}{2}, \frac{n-M}{2}, S, M) \\ &= (2S+1) \frac{(n-M-i)!}{(n+S+1)!} \sum_{V} (-1)^{i-V} \frac{(n+M-i+V)!}{V!(i-V)!(S-M-V)!(n-S-i+V)!} & (3.16) \\ &= (2S+1) \frac{(n-M-i)!}{(S-M)!} \sum_{V} (-1)^{V} \frac{\{(S-M+V)!\}^2}{V!(S-M+V-i)!(n-S-V)!(2S+1+V)!} & (3.17) \end{split}$$

It is convenient to use the expression (3.16) in calculating the values $C_{S,i}$ for some special cases. For example,

$$c_{S,0} = (2S+1)\frac{(n-M)!(n+M)!}{(n+S+1)!(n-S)!},$$

$$c_{M,i} = (2M+1)\frac{i!(n+M-i)!}{(n+M+1)!},$$

$$c_{n,i} = \frac{(n+M)!(n-M)!}{(2n)!}.$$

4. APPLICATION TO A SINGLE-DETERMINANT WAVE FUNCTION

When a wave function Φ is a single-determinant wave function, the space part $\Psi(\mathbf{I}_1, \mathbf{I}_2, \cdots, \mathbf{I}_N)$ is a product of one-electron functions:

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N) = \Psi_1(\mathbf{r}_1)\Psi_2(\mathbf{r}_2)\cdots\Psi_N(\mathbf{r}_N). \tag{4.1}$$

We denote orbitals associated with a-spins by $\phi_1, \phi_2, \ldots, \phi_{n+M}$ and those with β -spins by $\phi_1, \phi_2, \ldots, \phi_{n-M}$. Without changing the total wave function Φ , we can transform the orbitals $\{\phi\}$ and $\{\phi\}$ to $\{\phi'\}$ and $\{\phi'\}$ so that the only overlap remaining is between the pairs ϕ_i and ϕ_i

$$\begin{array}{ll} \varphi_{i}^{+} &= \sum\limits_{j=1}^{n+M} a_{ij} \; \varphi_{j} \; , & i=1,2,\cdots,n+M \; , \\ \varphi_{i}^{-} &= \sum\limits_{j=1}^{n-M} b_{ij} \; \varphi_{j} \; , & i=1,2,\cdots,n-M \; , \\ \langle \varphi_{i}^{+}, \varphi_{j}^{+} \rangle = \langle \varphi_{i}^{+}, \varphi_{j}^{+} \rangle = \delta_{ij} \; , \\ \langle \varphi_{i}^{+}, \varphi_{j}^{+} \rangle = \delta_{ij} \; \sqrt{\lambda_{i}} \; , & \lambda_{i} \geq 0 \; . \end{array} \right\} \; (4.2)$$

Using these transformed orbitals for the space part Ψ , we find that the inner product $\langle \Psi, P^{x}\Psi \rangle$ vanishes except when P^{x} is a product of some

interchanges of the pairs $\{\phi_i', \phi_i'\}$. When P interchanges the electrons of t pairs $\{\phi_{k1}', \phi_{k1}'\}$, $\{\phi_{k2}', \phi_{k2}'\}$, ..., $\{\phi_{kt}', \phi_{kt}'\}$, we see that

$$\langle \Psi, P^{x} \Psi \rangle = \lambda_{k1} \lambda_{k2} \cdots \lambda_{kt}$$
,
 $\epsilon_{P} = (-1)^{t}$, (4.3)
 $i(P) = t$.

It follows from (2.11), (3.3) and (4.3) that

$$\omega_{S} = \sum_{k=0}^{n-M} (-1)^{k} A_{k} C_{S, k}, \qquad (4.4)$$

where A_k is defined by the coefficients of the polynomial

$$\prod_{k=1}^{n-M} (1 - \lambda_k x) = \sum_{k=0}^{n-M} (-1)^k A_k x^k.$$
 (4.5)

For example,

$$A_{0} = 1 ,$$

$$A_{1} = \sum_{k} \lambda_{k} ,$$

$$A_{2} = \frac{1}{2} \left(\sum_{k} \lambda_{k} \right)^{2} - \sum_{k} \lambda_{k}^{2} = \lambda_{1} \lambda_{2} + \lambda_{1} \lambda_{3} + \cdots + \lambda_{1} \lambda_{n-M} +$$

$$+ \lambda_{2} \lambda_{3} + \cdots + \lambda_{n-M-1} \lambda_{n-M} ,$$

$$A_{n-M} = \prod_{k} \lambda_{k}$$
.

In order to calculate (4.4), it is convenient to introduce the following polynomial W(x):

$$W(x) = \prod_{k=1}^{n-M} \{1 - (1 - \lambda_k)x\} = \sum_{k=0}^{n-M} (-1)^k B_k x^k.$$
 (4.6)

By comparing (4.5) and (4.6), it is found that

$$A_{k} = \sum_{j=0}^{k} (-1)^{j} \frac{(n-M-j)!}{(n-M-k)!(k-j)!} B_{j}.$$
 (4.7)

The weights $\omega_S^{}$ of a single-determinant wave function are, therefore, expressed as

$$\omega_{S} = \sum_{k=0}^{n-M} \sum_{j=0}^{k} (-1)^{j+k} \frac{(n-M-j)!}{(n-M-k)! (k-j)!} B_{j} C_{S,k}$$

$$= (2S+1) \frac{(S+M)!}{(S-M)!} \sum_{v=0}^{n-S} \sum_{j=0}^{n-M} \sum_{k=j}^{N-M+v} (-1)^{v+j+k} \times \frac{\{(S-M+v)!\}^{2} (n-M-j)!}{(n-S-v)! (2S+1+v)! v! (k-j)! (S-M+v-k)!} B_{j}$$

$$= (2S+1) \frac{(S+M)!}{(S-M)!} \sum_{v=0}^{n-S} (-1)^{v} \frac{\{(S-M+v)!\}^{2}}{(2S+1+v)! v!} B_{S-M+v}.$$

$$(4.8)$$

This can be written as an integral,

$$\omega_{S} = (-1)^{S-M} \frac{2S+1}{(S-M)!} \int_{0}^{1} x^{S-M} (1-x)^{S+M} \frac{d^{S-M}W(x)}{dx^{S-M}} dx \qquad (4.9)$$

When W(x) is given, we can derive ω_S using the above equation (4.9). *)

The first order density matrix of the wave function under consideration has the following form:

$$\rho\left(\,\xi\,,\,\,\xi'\,\right) = \,\rho_{+}(\mathbf{r}\,,\mathbf{r}')\,\alpha(\sigma)\,\,\alpha(\sigma') + \,\rho_{-}(\mathbf{r}\,,\mathbf{r}'\,)\,\beta(\sigma)\,\,\beta(\sigma')\,,$$

Since the first order density matrix completely determines the original single-determinant wave function, it should also determine the weight ω_S . We derive an explicit expression for W(x) in terms of the first order density matrix. ω_S can be derived from W(x) by using eq. (4.9).

where

$$\rho_{+} = \sum_{i=1}^{n+M} \phi_{i}' \rangle \langle \phi_{i}' \rangle,$$

$$\rho_{-} = \sum_{i=1}^{n-M} \phi_{i}' \rangle \langle \phi_{i}' \rangle.$$

Since

$$\label{eq:polyspectrum} \langle \, \phi_i{}' \, , \, \{ (\, 1 \, - x \,) \, \rho_- + \, x \, \rho_- \rho_+ \, \} \, \phi_j{}' \, \rangle \; = \; \delta_{ij} \, \{ 1 \, - (1 \, - \lambda_i) \, x \} \; ,$$

W(x) can be expressed as an expectation value of an n-M particle operator K(x):

$$W(x) = \langle \Psi, K(x) \Psi \rangle$$

where

$$K (x: \mathbf{r}_{1}, \mathbf{r}_{2}, \dots, \mathbf{r}_{n-M}: \mathbf{r}_{1}', \mathbf{r}_{2}', \dots, \mathbf{r}_{n-M}') =$$

$$= \prod_{i=1}^{n-M} \{ (1-x)\rho_{-}(\mathbf{r}_{i}, \mathbf{r}_{i}') + x \rho_{-}\rho_{+}(\mathbf{r}_{i}, \mathbf{r}_{i}') \}$$

and

$$\Psi^{-}(\mathbf{r}_{1},\mathbf{r}_{2},\cdots,\mathbf{r}_{n-M}) = \sqrt{(n-M)!} \mathcal{A}\phi_{1}^{*}(\mathbf{r}_{1})\phi_{2}^{*}(\mathbf{r}_{2})\cdots\phi_{n-M}^{*}(\mathbf{r}_{n-M}).$$

It is seen that A'K(0) is a projection operator,

$$A K(0) = \Psi^{T} \wedge \Psi^{T}$$

and K(0) K(x) = K(x) . Therefore, we obtain an expression of W(x) in terms of ρ_+ and ρ_- only:

$$W(x) = \langle \Psi, K(x) \Psi \rangle = tr A K(0) K(x) = tr A K(x)$$
.

5. BEHAVIOUR OF $\omega_{_{\rm S}}$ FOR LARGE N

We discuss the case when all λ_k 's are equal to λ . Then

$$W(x) = \{1 - (1 - \lambda)x\}^{n - M}.$$
 (5.1)

Putting (5.1) into (4.9), we obtain

$$\omega_{S}(\lambda) = (2S+1)\frac{(n-M)!(1-\lambda)^{S-M}}{(S-M)!(n-S)!} \int_{0}^{1} x^{S-M} (1-x)^{S+M} \{1-(1-\lambda)x\}^{n-S} dx.$$
(5.2)

The asymptotic form of (5.2) is derived in the appendix when S - M is small compared with $N^{2/3}$,

$$\omega_{S}(\lambda) \sim \frac{(2S+1)(n-M)^{S-M}}{(1-\lambda)(n-M+\frac{2M}{1-\lambda})^{S-M+1}} \exp\left\{-\frac{1}{2(n-M)}(S-M-1)(S-M)-\frac{2M+(1-\lambda)^{2}(n-M)}{2\{2M+(1-\lambda)(n-M)\}^{2}}(S-M+1)(S-M+2)-\frac{\lambda}{2M+(1-\lambda)(n-M)}(S-M)(S-M+1)\right\}.$$
(5.3)

The equation (5.3) may be regarded valid over all possible values of S, since both left and right hand sides of (5.3) decrease rapidly as S - M becomes large compared with $N^{1/2}$.

5 a) Orthogonal case

Putting $\lambda = 0$ in the expression (5.2), we obtain

$$\omega_{S}(0) = (2S+1) \frac{(n+M)!(n-M)!}{(n-S)!(n+S+1)!}$$
 (5.4)

It is interesting to note that $\omega_S(0)$ is proportional to the number, $f_{n,S}$, of linearly independent spin functions for given n = N/2 and S,

$$\omega_{S}(0) = \frac{f_{n,S}}{\sum_{S'=M} f_{n,S'}}$$
 (5.5)

The asymptotic form of $\omega_{\hat{S}}(0)$ is, from (5.3),

$$\omega_{S}(0) \sim (2S+1) \frac{(n-M)^{S-M}}{(n+M)^{S-M+1}} exp \left\{ \frac{1}{2(n-M)} (S-M-1)(S-M) - \frac{1}{2(n+M)} (S-M+1)(S-M+2) \right\}.$$
(5.6)

For M = k n (0 < k < 1), ω_S can be approximated by a geometrical sequence,

$$\omega_{s} \sim (2S+1)\frac{(n-M)^{S-M}}{(n+M)^{S-M+1}} \sim \frac{2k}{1+k} \left(\frac{1-k}{1+k}\right)^{S-M}$$
 (5.7)

It should be noted that (5.7) does not contain the number of electrons explicitly. Therefore, for a fixed k, ω_S does not change much when N increases.

For
$$M = 0$$
,

$$\omega_{S} \sim \frac{(2S+1)}{n} e^{xp(-\frac{S^{2}+S+1}{n})}$$
 (5.8)

From (5.8), the expectation values of S, S^2 and S^3 can be calculated as \dagger)

$$\langle S \rangle = \sum S \omega_{S} \sim \int \frac{2S^{2}}{n} \exp(-\frac{S^{2}}{n}) dS = \sqrt{n\pi}/2 .$$

$$\langle S^{2} \rangle = \sum S^{2} \omega_{S} \sim \int \frac{2S^{3}}{n} \exp(-\frac{S^{2}}{n}) dS = n .$$

$$\langle S^{3} \rangle = \sum S^{3} \omega_{S} \sim \int \frac{2S^{4}}{n} \exp(-\frac{S^{2}}{n}) dS = 3\sqrt{n^{3}\pi}/4 .$$

The exact values are as follows, $\langle S \rangle = \frac{1}{2} + \frac{2^{2n-1}(n!)^2}{(2n)!},$ $\langle S^2 \rangle = n+1-\langle S \rangle,$ $\langle S^3 \rangle = -\frac{1}{4} + \frac{2^{2n-2}(6n-5) n(n!)^2}{(2n+1)!}$

In figures 1 and 2, ω_S is plotted as a function of S and S/n respectively for N = 10, 100 and 1000, using (5.8). We see from these figures that when N increases, ω_S spreads towards bigger N . However, for large N , appreciable weight ω_S is localized around the value S_{max} $\sim 0.5 \sqrt{\rm N}$. The second moment of the distribution around the average < S >

$$\langle S^2 \rangle - \langle S \rangle^2 \sim (1 - \frac{\pi}{4}) n \sim 0.107 N$$
.

5 b) Non-orthogonal case

For $M \neq 0$.

$$\omega_{s}(n,M,\lambda) \sim \omega_{s}\{(1-\lambda)(n-M)+M,M,0\}.$$
 (5.9)

since the factor $(2S+1)(n-M)^{S-M}/(1-\lambda)(n-M+2M/1-\lambda)^{S-M+1}$ decreases rapidly compared with the exponential part in (5.3), which may therefore be regarded as 1 .

For
$$M = 0$$
,
 $\omega_{S}(n,0,\lambda) \sim \frac{2S+1}{(1-\lambda)n} \exp\left(-\frac{S^{2}+S+1-\lambda}{(1-\lambda)n}\right)$

$$\sim \omega_{S}\left\{(1-\lambda)n,0,0\right\}.$$
(5.10)

It follows from (5.9) and (5.10) that the weight in the non-orthogonal case for N electrons can be approximated by the weight for $2\{(1-\lambda)(n-M)+M\}$ electrons in the orthogonal case:

$$\omega_{s}(n,M,\lambda) \sim \omega_{s}\{(1-\lambda)(n-M)+M,M,0\}$$
 (5.11)

(5.10)

When the overlap \(\lambda \) increases, the distribution shrinks. This can be seen from figures 3 and 4, where $\,\omega_{_{\hbox{\scriptsize S}}}^{}\,$ for some $\,\lambda\,$ values are plotted as a function of S for M = 0 and M = 0.2 n respectively.

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APPENDIX

We define a function I by the integral,

$$I_{\alpha,\beta,\gamma}(z) \equiv \frac{1}{\alpha!} \int_{0}^{1} x^{\alpha} (1-x)^{\beta} (1-z)^{\gamma} dx$$
 (A.1)

Then the weight (5.2) can be expressed as

$$\omega_{S}(\lambda) = (2S+1)\frac{(n-M)!(1-\lambda)^{S-M}}{(n-S)!}I_{S-M,S+M,n-S}(1-\lambda). (A.2)$$

The maximum of the integrand in (A. 1) is given by one of the roots of the following equation,

$$\frac{\alpha}{x_0} - \frac{\beta}{1 - x_0} - \frac{z \gamma}{1 - z x_0} = 0 . \tag{A.3}$$

Therefore,

$$x_0 = \frac{(1+z)\alpha + \beta + z\gamma - \sqrt{((1+z)\alpha + \beta + z\gamma)^2 - 4\alpha z(\alpha + \beta + \gamma)}}{2z(\alpha + \beta + \gamma)}.$$
 (A.4)

The order of x_0 is the same as $\alpha/\beta + z\gamma$.

Expanding $(1-x)^{\beta}(1-zx)^{\gamma} \exp \frac{\alpha x}{x_0}$ in terms of $x-x_0$, we obtain

$$\frac{1}{\alpha!} x^{\alpha} (1-x)^{\beta} (1-zx)^{\gamma} =$$

$$= \{a_0 + a_2(x-x_0)^2 + a_3(x-x_0)^3 + \cdots\} \frac{x^{\alpha}}{\alpha!} \exp(-\alpha x/x_0)^{(A.5)}$$

Here

$$a_0 = (1 - x_0)^{\beta} (1 - z x_0)^{\gamma} \exp \alpha ,$$

$$a_2 = -\frac{a_0}{2} \left(\frac{\beta}{(1 - x_0)^2} + \frac{z^2 \gamma}{(1 - z x_0)^2} \right) .$$
(A.6)

and

$$a_k = a_0 O(\alpha^{\left[\frac{k}{2}\right]} x_0^{-\left[\frac{k}{2}\right]})$$
 (A.7)

Integrating (A.5) over the range $(x = 0, x = \infty)$, we arrive at an asymptotic expansion

$$I \sim a_0 b_0 + a_2 b_2 + \cdots$$
 (A.8)

where

$$b_{k} = \frac{1}{\alpha!} \int_{0}^{\infty} (x - x_{0})^{k} \exp(-\alpha x / x_{0}) dx, \qquad (A.9)$$

$$b_{0} = (x_{0} / \alpha)^{\alpha+1},$$

$$b_{2} = b_{0} x_{0}^{2} (\alpha+2) / \alpha^{2}, \qquad (A.10)$$

$$b_k = b_0 O(x_0^k \alpha^{-\left[\frac{k+1}{2}\right]})$$
 (A.11)

From (A.5), (A.7) and (A.11), we find the order of magnitude of $a_k^{}b_k^{}$:

$$a_{k} b_{k}/a_{0} b_{0} = \begin{cases} O(x_{0}^{\frac{k}{2}}) & k : \text{ even .} \\ O(x_{0}^{\frac{k-1}{2}}/\beta + z \gamma) & k : \text{ odd .} \end{cases}$$
 (A.12)

Remembering that the order of x_0 is the same as that of $\alpha/\beta + z\gamma$ and using (A.12), we can take the first two terms in (A.8) in order to calculate log ω_0 with the accuracy of order $(\beta + Z\gamma)^{-1}$. Then we obtain

$$I \sim \left(1 - \frac{x_0^2 (\alpha + 2)}{2 \alpha^2} \left\{ \frac{\beta}{(1 - x_0)^2} + \frac{z^2 \gamma}{(1 - z x_0)^2} \right\} \right) \times \frac{x_0^{\alpha + 1}}{\alpha^{\alpha + 1}} (1 - x_0)^{\beta} (1 - z x_0)^{\gamma} \exp \alpha.$$
(A.13)

The expression (A.13) is substituted into (A.2), and after some manipulation, we obtain (5.3).

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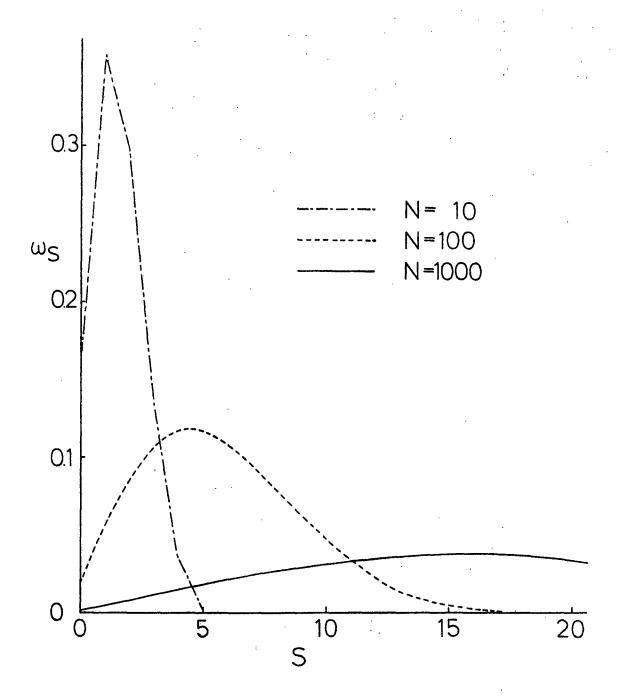


Figure 1. The weights $\omega_{s}(0)$ as a function of S.

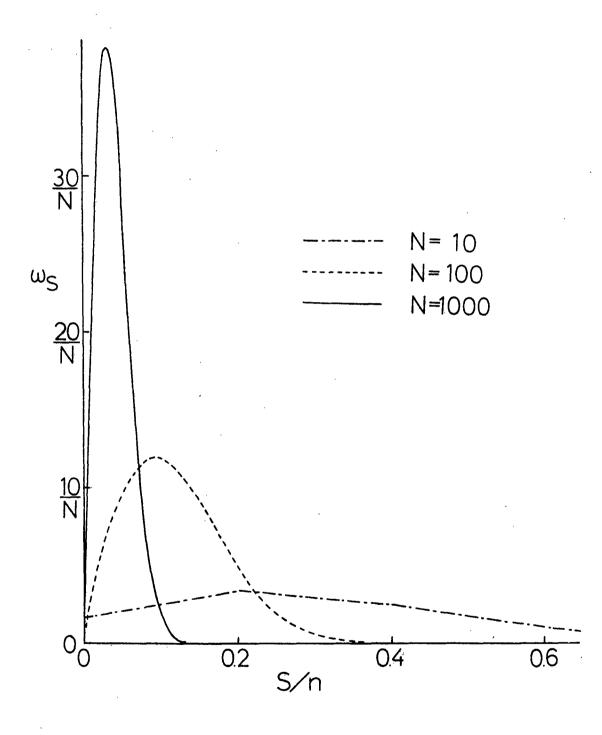


Figure 2 The weights $\omega_g(0)$ as a function of S/n.

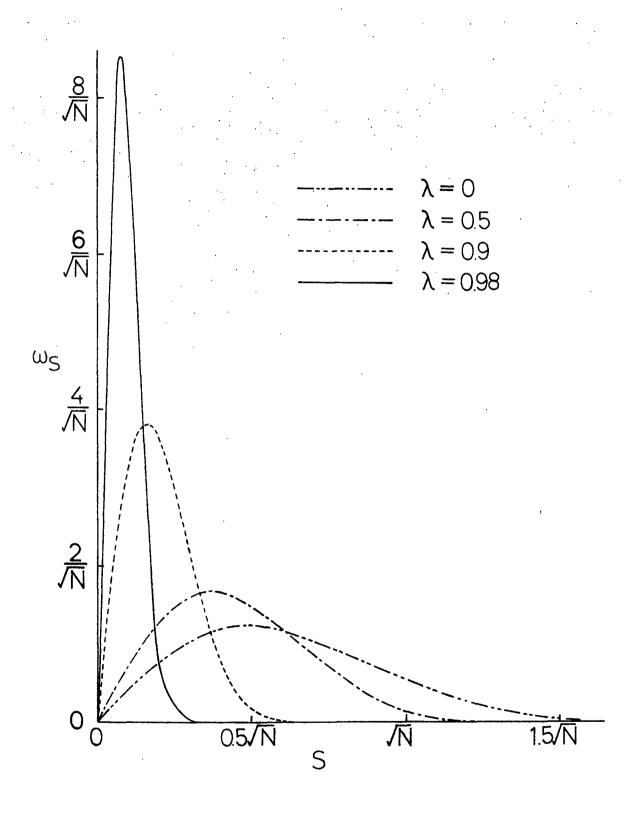


Figure 3 The weights ω_s as a function of S when M=0 for several values of the overlap integral.

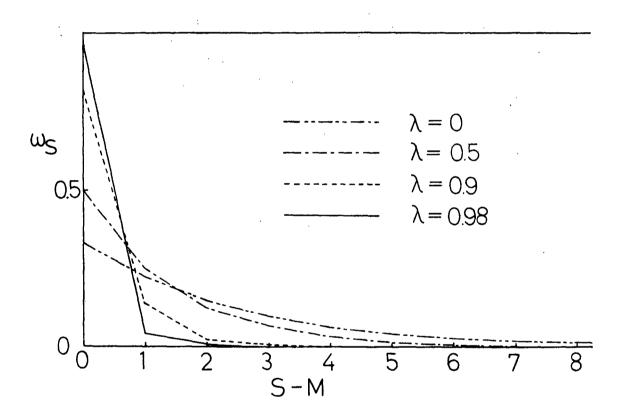


Figure 4 The weights ω_s as a function of S-M when M = 0.2 n for several values of the overlap integral.

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